

Water Rock Interaction [WRI 14]**Impact of supercritical CO₂/water interaction on the caprock nanoporous structure**

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Abstract

In the context of CO₂ geological storage, storage capacity and safety are two aspects to be evaluated in order to ensure the efficiency of this operation. The safety of this technique is primarily related to the conservation of the intrinsic properties of the caprock (stratigraphic trapping), which are controlled by the porous structure. This paper focuses on the assessment of the impact caused by the CO₂/water interaction on the porous nanostructure. A suspension of crushed rock samples and synthetic water was reacted with supercritical CO₂ at 84 bar and 53 °C under static conditions over a 2-month period. At the end of the experiment, the solid and liquid phases were collected in order to analyze the porous structure of the rock and water chemistry. Over short time periods, the results show a slight increase of the microporous and mesoporous volumes due to the rapid dissolution of calcite compared to the slower dissolution of aluminosilicates.

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1. Introduction

CO₂ geological storage is a technique considered to reduce accumulation of this gas in the atmosphere due to human activities. This technique involves CO₂ underground injection in reservoir formations with a high storage capacity (coal seams, gas and oil reservoirs and deep saline aquifers). Deep saline aquifers are a promising alternative due to their high storage capacity and the different mechanisms of trapping that are involved (hydrodynamic, solubility and mineral).

CO₂ would be sequestered as a high-density fluid allowing storage of important volumetric quantities.

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Even if supercritical CO₂ has a high density, interstitial water is denser causing an accumulation of CO₂ at the interface between reservoir and caprock. Once at the interface, CO₂ can penetrate the caprock by diffusion transport, forced drainage or through fractures [1,2]. These transport mechanisms are controlled by porous structure of caprock, which can be modified by CO₂/interstitial water interactions. The aim of this work is to evaluate the impact on the nanoporous structure induced by this interaction.

2. Materials and methods

2.1. Initial sample mineralogy characterization

Rock used in this study was sampled from the Tournemire underground tunnel, which is located in a Mesozoic marine basin on the southern border of the French Massif Central. The formation of interest consists in three mainly levels of marls and shales of the Toarcian and Domerian ages [3,4]. Toarcian layer is subdivided in three sublevels named upper, middle and lower. Our sample was taken from the lower Toarcian at 131.79 m depth.

The sample of the Tournemire formation was chosen as a caprock analogue because it has very interesting petrophysical properties and high resistance to the transport mechanisms.

Mineral identification and semi quantification were carried up by XRD techniques. Oriented and disoriented XRD have been conducted in order to identify global composition of the mineral cortege and clay phases respectively. Disoriented analysis showed a predominance of calcite (43%) and quartz (15.5%) as well as the presence of other crystallized phases as feldspar and pyrite in minor quantities. With regards to clay minerals: micas, kaolinite and chlorite were identified with predominance of micaceous phases.

2.2. Initial porous structure characterization

Porous structure characterization was carried out by using N₂ volumetric adsorption at low pressure (0-1 bar). This technique allows for exploring porous structure at nanometric scale. Analysis of the porous structure is based on IUPAC classification [5,6], which relates the pore size distribution with different thermodynamic mechanisms taking place in adsorption processes. According to this classification, analyses of microporosity and mesoporosity have been conducted using Dubinin Stoeckli and BJH (Barrett, Joyner and Halenda) models respectively [7-10]. Adsorption tests were conducted several times, which highlights the high reproducibility of our experiments.

2.3. Characterization of supercritical CO₂/water/caprock interaction in batch reactor

After initial characterization, sample and synthetic water were introduced into a high-pressure batch reactor. A Teflon vessel is used in order to avoid iron release from the reactor. CO₂ of high purity (99.9%) was then injected at 84 bar by using a compression system. Temperature was kept constant at 53°C through the use of an oil bath. Temperature and pressure inside the reactor were monitored during the whole experiment. A diagram of the experimental device is shown in fig. 1.

Two months later, the reactor was opened and the suspension was centrifuged in order to separate solid and liquid phases. Water was filtered by using a 0.2 µm filter before analysis. Cations, anions, and traces elements were quantified by atomic absorption spectroscopy, ionic chromatography and ICP-MS respectively. Porous structure analyses were also performed on rock sample taken from the batch reactor.

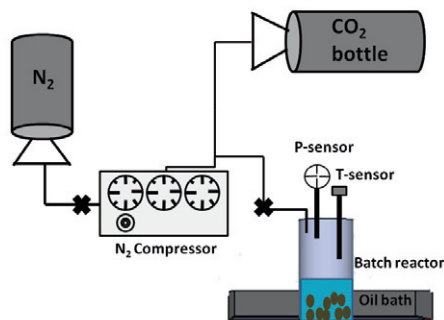


Fig. 1. Experimental device used to simulate supercritical CO₂/water/caprock interaction.

3. Results and discussion

Adsorption/desorption isotherms of the Tournemire shale are of type IV according to IUPAC classification. This type of isotherms exhibits a hysteresis loop, which highlights the presence of mesoporosity as a result of capillary condensation. However, it does not indicate the absence of microporosity.

The porosity in the sample seems in fact to be a combination between isotherms of type I and IV (see figure 2, left), which defines a bimodal medium at the working scale (nanometer scale). The presence of microporosity has been confirmed using the Dubinin/Stoeckli model. Pore size distributions have been determined by applying thermodynamic models adapted to each pore size range as mentioned in section 2.2. Pore size distributions before and after experiment in batch reactor are depicted in fig. 2 (right).

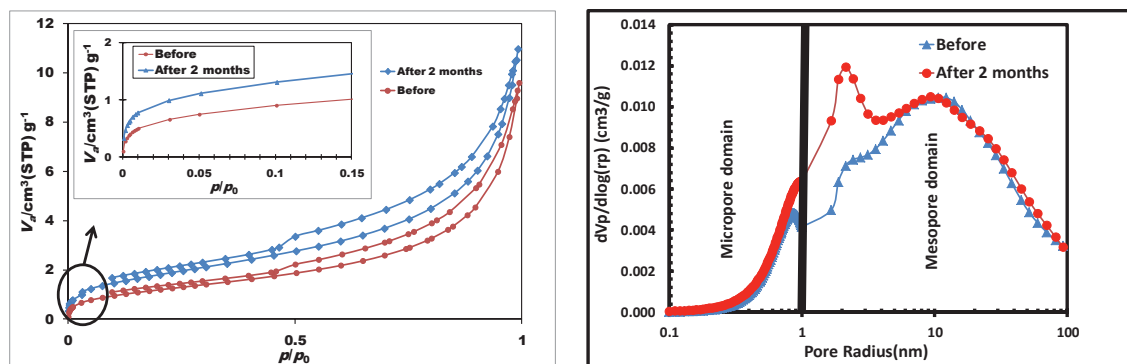


Fig. 2. Adsorption/Desorption isotherms before and after 2 months (left); micro and mesopores size distribution before and after 2 months (right). V_a : adsorbed volume, P_0 : saturation pressure, V_p : porous volume, r_p : pore radius.

After 60 days in batch reactor, an increase was observed in the number of pores lower than 10 nm. Micropore size distribution displays an increase of pore sizes between 0.7 and 0.9 nm as well as a shift in average pore distribution. In the case of mesopores, this increase was observed with pore sizes up to 10 nm. Experimental errors during adsorption tests are very low as attested by high reproducibility of the adsorption isotherms before CO₂/water/caprock interaction. We understand the variation in porous structure as the result of CO₂/water interaction. Changes in the nanoporosity are attributed to dissolution

of minerals, primarily calcite and also aluminosilicates as shown from variation of water chemistry presented in table 1. The increase of most elements in solution corroborates the contribution of most aluminosilicates detected using XRD. Decrease in sulfate concentration is indicative of possible gypsum precipitation (CaSO_4), as a result of sulfate complexation with calcium released by calcite dissolution.

Table 1. Chemistry water compositions before and after a 2-month residence time in a batch reactor.

Chemical element	Before (mg/l)	After (mg/l)
Ca	171	200
Mg	70.9	110
Na	997	1110
K	75	113
Si	0.01	38
Al	----	----
SO_4	2460	1125
Cl	593	560
HCO	----	1897

4. Conclusion.

This study has allowed us to evaluate the impact of CO_2 /water/rock interaction on nanoporosity of a caprock sample by using adsorption techniques. In this study, the application of adapted thermodynamic models has allowed us to evidence the impact on micro- and mesopores. Changes in water composition before and after experiment in batch reactor are coherent with calcite and aluminosilicate dissolution, which leads to the increase in the pore volume of our sample.

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